JOURNAL OF MATERIALS SCIENCE 9 (1974) 1602–1608

The direct piezoelectric effect in extruded polyethylene

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It has been shown that the direct piezoelectric effect occurs in low density, extruded polyethylene cable insulators and a piezoelectric *d* constant typical for such samples has been evaluated. Heat-treatment of the polyethylene, and oil absorption into it, both reduced the level of charge output. A probable mechanism for the piezoelectric effect in these polyethylene samples is given.

1. Introduction

The direct piezoelectric effect has previously been reported in polymer elastomers such as polyvinylidene fluoride [1] and PMMA [2] as well as polyethylene [3]. Following the observation of the inverse piezoelectric effect in polyethylene when a direction of anisotropy was imposed on the material by an electric field [4], it was expected that the direct piezoelectric effect ought to be apparent in material that was mechanically oriented. It was felt likely that low density polyethylene cable insulators would be in such a condition due to the extrusion process used to fabricate them, and also that they would contain polar impurities. They might, therefore, exhibit the direct piezoelectric effect.

The present work has shown that the piezoelectric effect does occur in such polyethylene and some effort has been made to establish the origin of the charge producing mechanisms. It is known that low density polyethylene is made up of about 50% crystalline regions, the remainder being amorphous material. The crystalline material may take many forms, lamellae, spherulites and fibrilar "shish-kebabs" have all been produced in laboratory-grown samples [5] and at first sight it would appear that the crystalline regions would show preferential orientation and be the origin of the piezoelectric effect. However, it has been shown that this is not so, and that the effect must originate in the amorphous regions. In order for the piezoelectric effect to occur, the amorphous regions must, therefore, be anisotropic and a model has been proposed along these lines. The results that have been obtained have enabled a piezoelectric constant to be evaluated for the material and have supported the proposed model.

2. The hydrostatic test tank

2.1. Apparatus

The apparatus was designed so that polyethylene cable samples could be immersed in a fluid and subjected to a varying pressure. The frequency was chosen such that the wavelength was long compared to the length of the sample, so that the pressure on the sample at any instant was spatially constant.

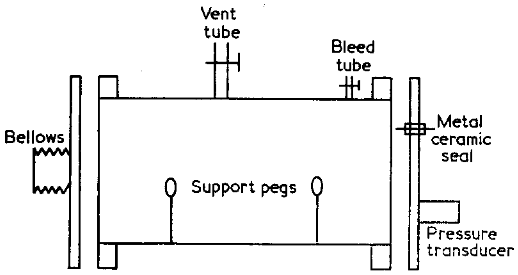

Figure 1 Hydrostatic test tank.

The test tank, shown in Fig. 1, consisted of a 10 cm diameter copper tube of length 22.5 cm fitted with two air bleed tubes, two axial support pegs to hold a polyethylene cable insulator sample and a brass sealing flange at each end. One end plate was fitted with a bellows which

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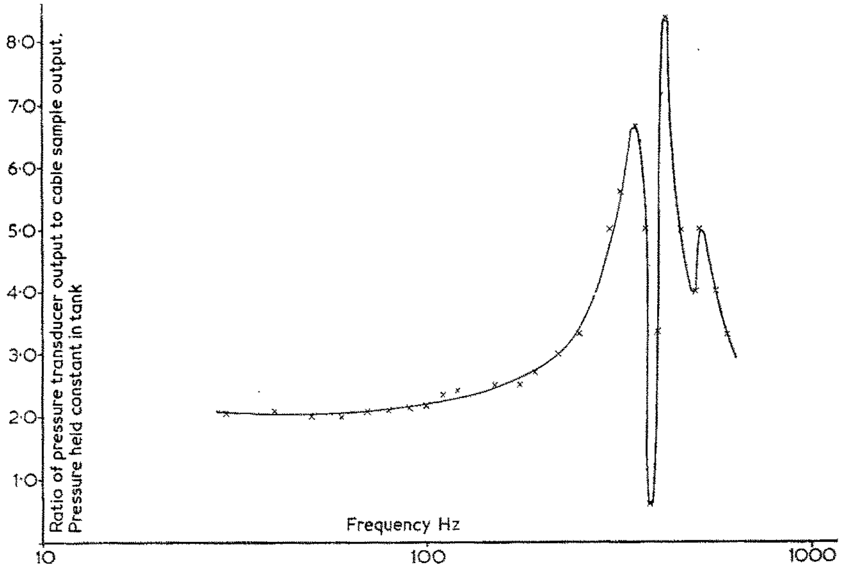

Figure 2 Frequency response of hydrostatic test tank.

was driven by a mechanical vibrator and the other end plate contained four metal ceramic seals and a strain gauge type pressure transducer. The metal ceramic seals enabled outputs to be taken from the sample in the tank. A charge-sensitive amplifier with sensitivity 10^{11} V C^{-1} amplified the output before it was displayed on an oscilloscope.

Extruded polyethylene samples were taken from a cable, and they had a conducting antimicrophonic layer to which electrical contact could be made.

2.2. Initial checks on the system

In order that mechanical resonances in the system might be avoided, output from a cable sample was monitored against frequency for a constant drive voltage. The results are shown in Fig. 2. Further measurements on insulator samples were carried out at 70 Hz because the system response was relatively insensitive to frequency at this point.

It was confirmed that the output being observed was due to the pressure within the tank, and not due to electrical crosstalk, by disconnecting the drive linkage between the vibrator and the bellows. The output fell to zero when this was done. A further check on the system was carried out with a piece of PZT5A piezoelectric ceramic (supplied by Brush Clevite), and a plot of PZT output versus pressure transducer output is shown in Fig. 3; (a transducer output of 250 mV corresponds to a pressure in the tank of 8.175×10^3 N m^{-2}). The piezoelectric d constant is defined as:

$$d = \frac{\text{charge produced/unit area}}{\text{stress applied}}$$

and it is known that the hydrostatic constant d_h for this material is 32×10^{-12} C N^{-1}. The area of the ceramic used was $0.8\ 10^{-4}$ m^2 and, therefore, by using the results shown in Fig. 3 the constant may be calculated to be 29×10^{-12} C N^{-1}. This is within the expected experimental error.

2.3. Low density extruded polyethylene samples under hydrostatic pressure

The extruded polyethylene samples were placed in the tank and earthed contact made to the antimicrophonic layer which is in intimate contact with the polyethylene. Output was then observed from the centre conductor, and a typical plot of cable output versus output from the pressure transducer is shown in Fig. 4. Using these data, the piezoelectric constant was evaluated to be $d_h \simeq 10^{-13}$ C N^{-1}. Very few values of this constant for polymer materials are available in the literature; however, Fukada and Takaskita [1] reported $d_{31} = 3.7 \times 10^{-12}$ C N^{-1} and $d_{32} = 2.2 \times 10^{-13}$ C N^{-1} for polyvinylidene fluoride and Date *et al.* [6] obtained a value of

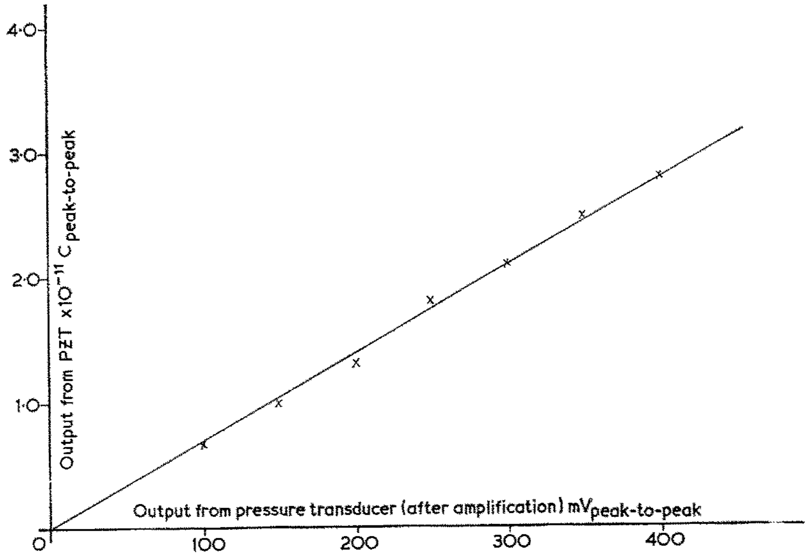

Figure 3 PZT output versus pressure transducer output.

d_{25} of approximately 10^{-12} C N^{-1} for orientated poly (γ-methyl, L-glutamate). The above value of d_h for polyethylene is comparable with these figures.

It was assumed that the piezoelectric output was dependent upon some orientation phenomenon in the polyethylene. Thus by heating the polyethylene close to its melting point, it was felt that a relaxation of this orientation might occur and thus that the piezoelectric output could be decreased. The sample was, therefore, heated at 110°C for 1 h and retested. As shown in Fig. 4, the charge output was found to have been reduced by a factor of 5.

The assumption that the material was oriented was also justified during the course of these heat-treatments by observing the dimensional changes which occurred in the samples. The polyethylene insulator was removed from a sample of the cable. The anti-microphonic layer

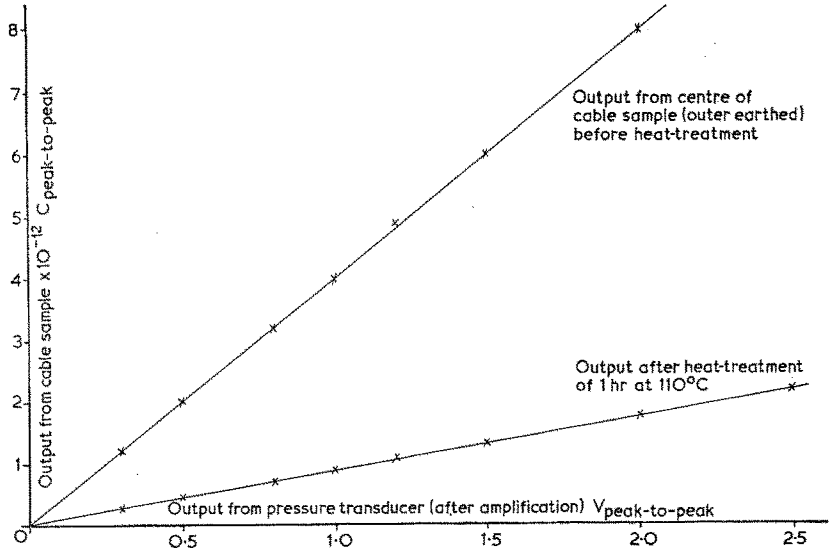

Figure 4 Typical cable insulator output before and afterheat-treatment.

TABLE I

	Initial diameter (cm)	Initial length (cm)	Final diameter (cm)	Final length (cm)
Sample 1	0.254	5.367	0.262	5.117
Sample 2	0.254	5.116	0.262	4.876

and the copper centre conductor were both removed and the polyethylene was, therefore, unconstrained and free to move in any direction. The sample dimensions were then measured; it was heated for a period of several hours, and its dimensions were remeasured. The results of such an experiment on two samples are shown in Table I. In each case the length decreased by 4.7% and the diameter increased by 3.2%. The volumes remained constant to within 1%. This conclusively showed that the samples were oriented in the direction of extrusion.

3. X-ray diffraction of low density polyethylene cable samples

Low density polyethylene consists of approximately 50% crystalline material in an amorphous matrix. Any preferred orientation of the crystallites should thus be revealed by a break-up in the Debye rings obtained from a transmission Läue X-ray photograph of the specimen [7]. The results presented in Section 2.3 lead to the conclusion that the material is preferentially oriented and one would intuitively assume that it is the crystalline regions which are anisotropic. Thus, to check this 1 mm thick samples were cut in planes perpendicular and parallel to the direction of extrusion of a piezoelectrically active polyethylene specimen. A typical X-ray diffraction picture is shown in Fig. 5, and although the sharp Debye rings show the presence of a significant amount of crystalline material, there is no tendency for the rings to break up and thus no indication of any preferred orientation in the crystallites.

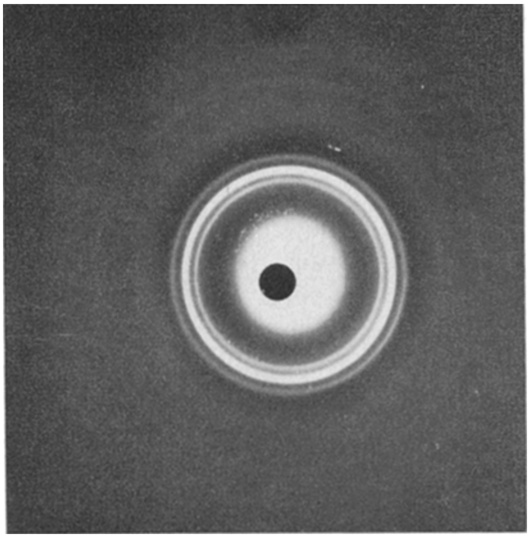

Figure 5 X-ray of polyethylene cable insulator.

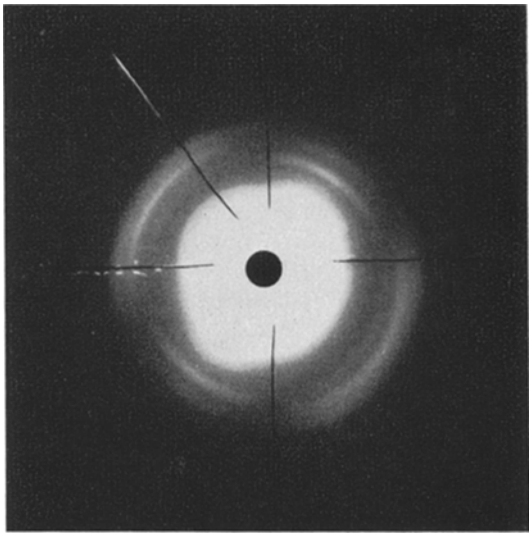

Figure 6 X-ray of cold drawn polyethylene.

By comparison, Fig. 6 shows an X-ray picture of a sample of cold drawn low density polyethylene (draw ratio of 2). In this case distinct segmentation of the Debye rings has occurred and it is clear that there is a preferential orientation of the crystalline material.

These results show that the crystalline regions in the cable samples were not preferentially oriented. Therefore, any anisotropy and hence the origin of the piezoelectric effect must be in the amorphous regions.

4. Extruded polyethylene sample in transformer oil

It is known that polyethylene absorbs organic liquids, particularly oils, into the amorphous regions and it was expected that this absorption would lead to relaxation of any orientation in these regions [8]. Hence the effect of oil on the piezoelectric output should provide further information on the origin of the piezoelectric effect in the material. The tank was, therefore, filled with transformer oil and a sample of

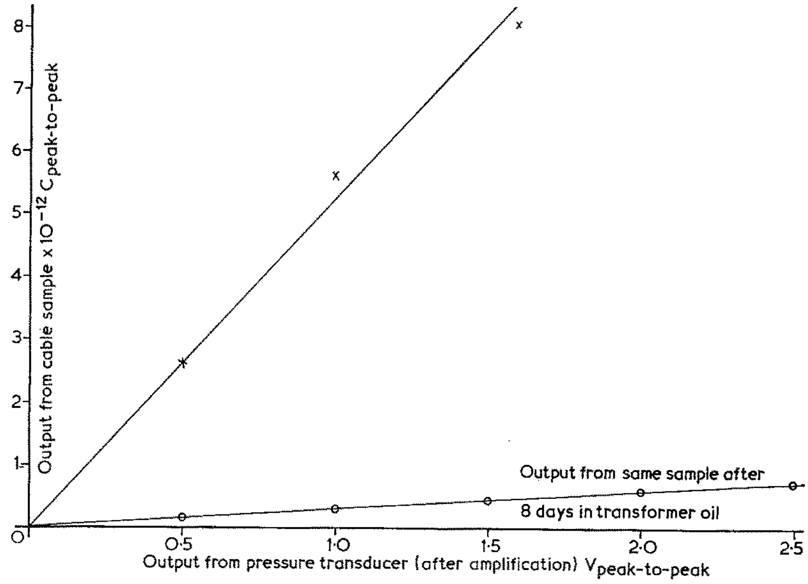

Figure 7 Cable insulator output before and after oil absorption.

extruded polyethylene cable insulator was placed in it. The output was recorded from the sample and it was then left in the oil for 8 days and retested. The charge output had decreased by a factor of about 8, as shown in Fig. 7.

These results indicate that there is indeed anisotropy in the amorphous regions and that randomisation of this alignment causes the piezoelectric effect to decrease.

5. Estimate of the concentration of polar impurities in the amorphous regions required to give rise to the observed charge from polyethylene

Aligned polar groups in the amorphous regions are a probable source of the charge producing mechanism. It is worthwhile considering the concentration of such groups necessary to give a charge output equal to the one observed.

The model that will be considered consists of N_2 aligned dipolar groups m^{-3}, each with a polarizability $\alpha_2 + \mu_2^2/(3kT)$ in a medium of N_1 aligned CH_2 molecules m^{-3} each having a polarizability α_1. α_2 is the electronic contribution to the polarizability of the polar group and α_1 is the electronic contribution for the polyethylene. It is known [9] that the average value of the dipolar polarizability, $\mu\langle\cos\theta\rangle/E$ in the direction of the applied field is equal to $\mu^2/(3kT)$ where k is Boltzmann's constant and T is the absolute temperature.

The permanent dipole moment, μ, for polyethylene is negligible but for a polar group the permanent dipole moment is large compared with α_2:

$$\therefore P = N_1\alpha_1 + N_2\frac{\mu_2^2}{3kT}E \qquad (1)$$

where P = dipole moment/unit volume, and E = the electric field.

The dipole moment/unit volume, P, is equivalent to the surface charge density [10] so that the ratio P/E may be readily evaluated from the experimental results.

In the assumed model, as alternating pressure is exerted on the material, the dipole separation increases causing charge separation and thereby increases the internal field E. There will be a radial field in the cylindrical insulator due to the assumed aligned polar groups along the polyethylene chain.

By considering a polyethylene cylinder it is known that

$$E_r = \frac{q_1}{2\pi r\epsilon_0\epsilon}$$

where E_r = the radial field; q_1 = the charge/unit length; r = radius; ϵ_0 = the permittivity of free space; ϵ = the relative permittivity of polyethylene.

The relative permittivity of polyethylene is given by [10] as:

$$\epsilon = \frac{10^3 + 0.65\rho}{10^3 - 0.325\rho}$$

where ρ = density of polyethylene in MKS units. For the low density polyethylene considered, $\rho = 918$ kg m^{-3} and hence: $\epsilon = 2.275$.

It was shown by Lorentz [11] that it was more valid to use the internal field, E_i, for the field in Equation 1 rather than the apparent external field, E, where:

$$E_i = \frac{\epsilon + 2}{3} E.$$

$$\therefore E_i = \frac{\epsilon + 2}{3} \cdot \frac{q}{2\pi r \epsilon_0 \epsilon}.$$

For the cylindrical geometry specimen consider the charge/unit area:

$$P = \frac{q}{2\pi r}.$$

Hence the ratio:

$$\frac{P}{E} = \frac{3\epsilon}{\epsilon + 2} \epsilon_0$$

It may be shown [12] that the polarisability α_1 for CH$_2$ molecules transverse to the chain axis is 2.05×10^{-30} m^3. The total number of "CH$_2$" molecules present is:

$$N_1 = \frac{\text{Avogadro's No.}}{\text{molecular weight}} \times \text{density} = 4 \times 10^{28}\,\text{m}^{-3}.$$

As $N_1\alpha_1\epsilon_0$ is small compared with P/E, it may be neglected so that:

$$N_2 = \frac{3kT}{\mu_2^2} \frac{P}{E}.$$

If we assume that the permanent dipole moment of the polar group is, say, three Debye units, i.e. 10^{-29} Cm [13], and knowing that kT is approximately 4×10^{-21} J, then:

$$N_2 = \frac{12 \times 10^{-21}}{10^{-58}} \cdot \frac{6.825}{4.275} \cdot \frac{1}{36\pi 10^9}\,\text{m}^{-3}$$

$$N_2 = 1.6 \times 10^{27}\,\text{m}^{-3}$$

i.e. the concentration of impurity dipole moments needs to be 4 mol %. It is likely that polar groups will tend to separate out into the amorphous regions so that this is a figure that will apply to the bulk polyethylene. This value is in reasonable agreement with the concentration of polar groups likely to be found in low density polyethylene [7].

6. Discussion and conclusions

It is known that the direct piezoelectric effect is dependent upon a direction of anisotropy in a material; charge separation occurring on the application of pressure. It has been demonstrated in this paper that charge production occurs when a direct pressure is exerted on extruded low-density polyethylene from cable insulators. Furthermore, a process which would tend to randomize any alignment in the material, i.e. a heat-treatment at 110°C, reduces the charge output. The results of the X-ray diffraction and the oil absorption both show, however, that the origin of the charge producing mechanism in the polyethylene is in the amorphous regions. It has been demonstrated that polar impurities could be responsible for the phenomenon.

It is to be expected that in the extrusion of the cable insulator, where the polyethylene leaves the die at high velocity and high temperature, some "streaming" of the long chain molecules will occur. When polyethylene crystallizes, then the residual effects of this streaming will only be apparent in the amorphous regions, where a certain proportion of the molecules will be oriented along the direction of extrusion. Impurities, some of which will be polar, will tend to separate out into the amorphous regions, so it is reasonable to assume that a certain amount of these will be associated with the aligned polyethylene chains. The basic requirement for a piezoelectric charge output is therefore established, i.e. oriented polar groups are present in the material. A simple calculation based on the likely dipole moments of dipole groups, shows that the concentration required is not unreasonable.

Acknowledgements

This work was carried out as part of the programme of the United Kingdom Atomic Energy Authority. The authors would like to thank Mr D. Harrison who originally suggested the possibility of piezoelectric phenomena in polyethylene insulated cables and Professor A. Keller of Bristol University for helpful discussions.

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Received 19 March and accepted 22 March 1974.